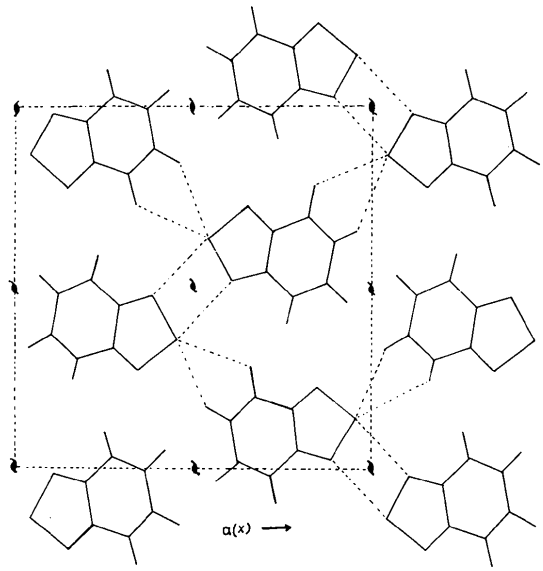

Fig. 3. Packing diagram of piaselenole molecules viewed down the *c* axis with an intricate network of short contacts.

also relatively shorter than the C=C double-bond distance. The other bond lengths including the Se—N bonds [1·792 (6) and 1·777 (6) Å] and angles are within the normal range found in similar heterocyclic systems. The molecules are planar with largest deviations from the least-squares plane of 0·017 (7) Å at N2 and N3 on opposite sides of the molecular plane. The small departure from C_{2v} symmetry of the molecule may be due to molecular packing forces. This is similar to that observed in the crystal structure of piaselenole–piaselenolium pentaiodide (Gieren, Hubner, Lamm, Neidlein & Droste, 1985) where protonation at one N of the SeN_2 unit also destroyed the molecular symmetry and led to significant changes in bond lengths and bond angles. In our case the probable partial protonation at the N atom results in lengthening of one Se—N bond. The crystal structure is characteristic of similar kinds of compounds like dibenzofuran (Banerjee, 1973) and indole (Roychowdhury & Basak, 1975) with a packing arrangement of pairs of localized molecules related by twofold symmetries and a network of short contacts. In piaselenole the Se···N contact distance in the parallelogram (Fig. 3) is 3·154 (4) Å. This distance is significantly shorter [2·972 (5) and 2·691 (4) Å] in the piaselenole–piaselenolium pentaiodide structure.

References

Banerjee, A. (1973). *Acta Cryst.* B**29**, 2070–2074.

Gieren, A., Hubner, T., Lamm, V., Neidlein, R. & Droste, D. (1985). *Z. Anorg. Allg. Chem.* **523**, 33–44.

Hinsberg, O. (1889). *Ber. Dtsch. Chem. Ges.* **22**, 2895–2902.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Luzzati, P. V. (1951). *Acta Cryst.* **4**, 193–200.

Rettig, W. & Wirz, J. (1976). *Helv. Chim. Acta*, **59**, 1054–1074.

Roychowdhury, P. & Basak, B. S. (1975). *Acta Cryst.* B**31**, 1559–1563.

Seal, A. & Roy, S. (1981). *Indian J. Phys.* **55**A, 414–416.

World List of Crystallographic Computer Programs (1973). *J. Appl. Cryst.* **6**, 309–346.

Zincke, E. C. T. & Schwartz, P. (1899). *Justus Liebigs Ann. Chem.* **307**, 28–49.

Acta Cryst. (1989). C**45**, 75–77

Structure of *endo,exo*-9,11-Dibromotricyclo[6.3.1.$0^{2,7}$]dodeca-2(7),3,5-trien-10-one

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Abstract. $C_{12}H_{10}Br_2O$, $M_r = 330\cdot04$, orthorhombic, $P2_12_12_1$, $a = 6\cdot045\,(2)$, $b = 9\cdot837\,(3)$, $c = 19\cdot487\,(7)$ Å, $V = 1159\,(1)$ Å^3, $Z = 4$, $D_x = 1\cdot89$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 69\cdot02$ cm^{-1}, $F(000) = 640$, $T = 295$ K, $R = 0\cdot053$ for 1348 observed reflections. The compound studied has a benzene ring fused to a bicyclo[3.2.1]octane ring. The two Br atoms are bonded to the seven-membered ring in *endo* and *exo* positions at two C atoms. Oxygen is also bonded to the same ring with a double C=O bond.

Introduction. Benzobarrelene (1,4-dihydro-1,4-ethenonaphthalene) is a molecule of considerable potential mechanistic interest in view of the di-π-methane rearrangement (Hixon, Mariano & Zimmerman, 1973). By the introduction of a substituent in a vinyl location the symmetry of the benzobarrelene skeleton is destroyed. On this basis, vinyl substituted benzobarrelenes gain more importance by elucidation of the mechanism of the $(2\pi + 2\pi)$-cycloaddition reaction and di-π-methane rearrangement. Recently, an

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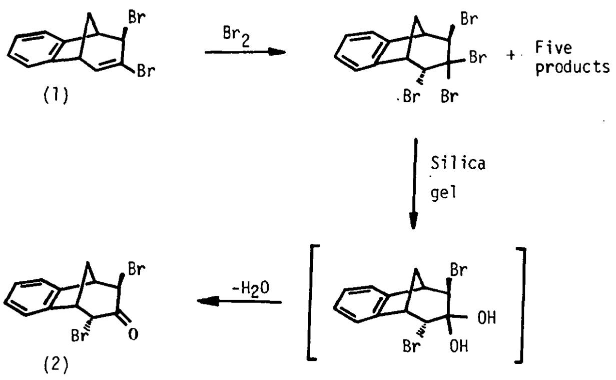
alternative large-scale preparation of monosubstituted benzobarrelenes has been developed (Balcı, Çakmak & Harmandar, 1985). As an extension of this work, the synthesis of disubstituted benzobarrelenes has been undertaken. To this end, the bromination of (1) has been carried out and after repeated column chromatography, six products have been isolated, one of which is the title compound (2). Here we describe the detailed X-ray analysis of this compound.



Experimental. Pale-yellow plates, 0·3 × 0·3 × 0·15 mm; Syntex $R3$ diffractometer, graphite-monochromatized Mo $K\alpha$; lattice parameters from setting angles of 25 reflections, $9 < 2\theta < 22°$; intensity data measured by ω-scan technique, variable scan speed: 2 to 12° min^{-1}, scan range from 0·9° below $K\alpha_1$ to 0·9° above $K\alpha_2$, background/scan ratio 0·5; 2927 reflections measured, $4·5 \leq 2\theta \leq 55°$, hkl range −7, 0, 0 to 7, 13, 26, 1348 unique reflections considered observed, $I \geq 3\sigma(I)$; two check reflections at intervals of 100, variation ±0·9%, intensities corrected for Lp with *XTAPE* (Sheldrick, 1983); numerical absorption correction with Gaussian integration (face-indexed) method applied, merging R value before correction $R_{\rm int} = 0·088$, after correction $R_{\rm int} = 0·038$, min. transmission 0·273, max. transmission 0·718. Structure solved by Patterson methods. Positions of Br atoms from Patterson map, other non-H atoms from Fourier map, all H atoms except the two of the CH_2 group from difference Fourier map. Refinement based on $|F|$ values carried out with block-cascade algorithm, non-H atoms anisotropically, the two H atoms of the CH_2 group with the geometrically calculated positions as fixed and the other H atoms isotropically refined. Final $R = 0·053$, $wR = 0·055$ with weighting scheme $w^{-1} = \sigma^2(F) - 0·001F^2$, $S = 1·455$, normal-probability-slope value 1·247; max. final shift-to-e.s.d. ratio 0·161, mean 0·037, max. and min. heights in final difference Fourier map 0·84 and −0·51 e Å^{-3}, all calculations performed with *SHELXTL* (Sheldrick, 1983) on a Nova 3 computer, scattering factors taken from *International Tables for X-ray Crystallography* (1974).

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3) *of the non*-H *atoms with e.s.d.'s in parentheses*

	x	y	z	$U_{\rm eq}$*
Br(2)	825 (3)	4390 (1)	6879 (1)	63 (1)
Br(1)	4346 (3)	1535 (1)	8973 (1)	74 (1)
C(1)	1245 (20)	3770 (11)	9002 (6)	52 (4)
C(2)	2393 (18)	2801 (10)	8504 (6)	45 (4)
C(3)	3662 (18)	3531 (11)	7934 (5)	42 (3)
C(4)	2660 (19)	4872 (11)	7681 (5)	43 (4)
C(5)	1334 (21)	5611 (13)	8229 (7)	55 (4)
C(8)	−304 (19)	4650 (13)	8563 (7)	61 (5)
C(7)	2843 (19)	4835 (11)	9250 (6)	44 (4)
C(6)	2887 (19)	5923 (11)	8803 (5)	43 (4)
C(9)	4235 (26)	7006 (10)	8921 (6)	53 (4)
C(10)	5580 (25)	6998 (12)	9494 (7)	56 (5)
C(11)	5629 (26)	5939 (12)	9949 (7)	58 (4)
C(12)	4180 (23)	4835 (11)	9843 (5)	51 (4)
O(1)	5352 (14)	3114 (8)	7698 (4)	61 (3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *involving the non*-H *atoms with e.s.d.'s in parentheses*

Br(2)—C(4)	1·975 (14)	Br(1)—C(2)	1·944 (13)
C(1)—C(2)	1·526 (17)	C(1)—C(8)	1·536 (18)
C(1)—C(7)	1·505 (17)	C(2)—C(3)	1·529 (16)
C(3)—C(4)	1·532 (16)	C(3)—O(1)	1·194 (14)
C(4)—C(5)	1·518 (18)	C(5)—C(8)	1·516 (19)
C(5)—C(6)	1·493 (18)	C(7)—C(6)	1·379 (16)
C(7)—C(12)	1·410 (17)	C(6)—C(9)	1·360 (17)
C(9)—C(10)	1·380 (20)	C(10)—C(11)	1·367 (18)
C(11)—C(12)	1·410 (19)		

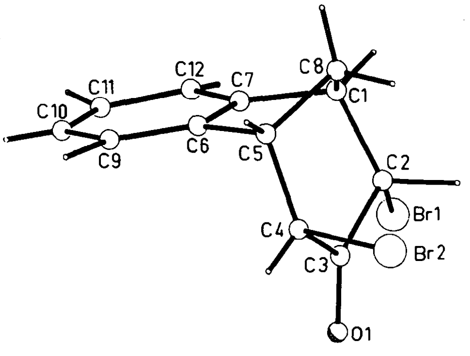


Fig. 1. Perspective view of the molecule with the labelling of the atoms.

Discussion. The final atomic coordinates with the equivalent isotropic temperature factors $U_{\rm eq}$ of the non-H atoms are listed in Table 1 according to the labelling system shown in Fig. 1. The bond lengths and angles of the non-H atoms are given in Table 2 and Table 3 respectively.* The C—C lengths of the benzene ring vary from 1·360 (17) to 1·410 (19) Å with a mean

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51296 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond angles* (°) *involving the non-*H *atoms with e.s.d.'s in parentheses*

C(2)—C(1)—C(8)	106·0 (10)	C(2)—C(1)—C(7)	110·1 (10)
C(8)—C(1)—C(7)	100·3 (9)	Br(1)—C(2)—C(1)	112·2 (8)
Br(1)—C(2)—C(3)	109·6 (8)	C(1)—C(2)—C(3)	113·4 (9)
C(2)—C(3)—C(4)	115·9 (9)	C(2)—C(3)—O(1)	123·4 (10)
C(4)—C(3)—O(1)	120·7 (10)	Br(2)—C(4)—C(3)	105·8 (7)
Br(2)—C(4)—C(5)	111·8 (8)	C(3)—C(4)—C(5)	113·3 (9)
C(4)—C(5)—C(8)	110·4 (11)	C(4)—C(5)—C(6)	106·9 (10)
C(8)—C(5)—C(6)	102·7 (10)	C(1)—C(8)—C(5)	101·0 (9)
C(1)—C(7)—C(6)	110·5 (10)	C(1)—C(7)—C(12)	129·2 (10)
C(6)—C(7)—C(12)	120·3 (11)	C(5)—C(6)—C(7)	107·5 (10)
C(5)—C(6)—C(9)	131·7 (11)	C(7)—C(6)—C(9)	120·8 (11)
C(6)—C(9)—C(10)	119·1 (11)	C(9)—C(10)—C(11)	122·7 (12)
C(10)—C(11)—C(12)	118·6 (13)	C(7)—C(12)—C(11)	118·5 (11)

value of 1·384 (18) Å, a little shorter than 1·395 Å, the characteristic bond length in an aromatic molecule. All of the other C—C single-bond lengths of the molecule range from 1·493 (18) to 1·536 (18) Å. C—Br bond lengths, 1·944 (13) and 1·975 (14) Å, agree with those observed in $C_{12}H_{11}Br_3$ (Ergin, Harmandar & Balcı, 1987; Büyükgüngör, Harmandar & Balcı, 1989). The length of the C=O double bond is 1·194 (14) Å, a little shorter than 1·23 Å, the characteristic double-bond length in cyclohexanone (*CRC Handbook of Chemistry and Physics,* 1979–1980). The three atoms attached to the C(3) atom lie in a plane with bond angles of 115·9 (9), 123·4 (10) and 120·7 (10)° (total 360·0°).

The molecule mainly consists of two non-planar carbon rings fused to the benzene ring at the C(6) and C(7) atoms and also sharing the two atoms C(1) and C(5). The C(1)—C(2)···C(5) plane makes angles of 101·5 and 99·9° with the C(1)—C(5)—C(6)—C(7) and benzene ring planes, respectively. This indicates that C(1) and C(5) lie nearly in the plane of the benzene ring.

In the refinement, the coordinates of the two H atoms of C(8) could not be found from the difference Fourier maps. This is probably due to the close proximity of the two Br atoms. For this reason, the positions of these H atoms were calculated geometrically and held fixed.

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References

Balci, M., Çakmak, O. & Harmandar, M. (1985). *Tetrahedron Lett.* **26**, 5469–5472.

Büyükgüngör, O., Harmandar, M. & Balci, M. (1989). *Acta Cryst.* C**45**, 77–79.

CRC Handbook of Chemistry and Physics (1979–1980). 60th ed. Cleveland, Ohio: CRC Press.

Ergin, Ö., Harmandar, M. & Balci, M. (1987). *Acta Cryst.* C**43**, 1621–1623.

Hixon, S. S., Mariano, P. S. & Zimmerman, H. E. (1973). *Chem. Rev.* **73**, 531–551.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Sheldrick, G. M. (1983). *SHELXTL User's Manual,* revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

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Structure of 9,10,10-Tribromotricyclo[6.3.1.$0^{2,7}$]dodeca-2(7),3,5-triene

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Abstract. $C_{12}H_{11}Br_3$, $M_r = 394{\cdot}97$, monoclinic, $C1c1$, $a = 10{\cdot}086\,(3)$, $b = 12{\cdot}302\,(4)$, $c = 10{\cdot}165\,(2)$ Å, $\beta = 102{\cdot}36\,(2)°$, $V = 1232\,(1)$ Å^3, $Z = 4$, $D_x = 2{\cdot}13$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 96{\cdot}96$ cm^{-1}, $F(000) = 752$, $T = 295$ K, $R = 0{\cdot}032$ for 1117 observed reflections. The compound studied has a benzene ring fused to a bicyclo[3.2.1]octane ring. The three Br atoms, one being in an *exo* position, are bonded to the seven-membered ring at two C atoms.

Introduction. In connection with our studies on bicyclic allenes and alkynes (Balcı & Harmandar, 1984) we were interested in the synthesis of (1). Therefore, we studied the bromination of 10-bromotricyclo[6.3.1.$0^{2,7}$]dodeca-2(7),3,5,9-tetraene (2). The bromination reaction was carried out at 273 and 223 K. Surprisingly, we obtained a completely different product distribution. From the reaction at 223 K we isolated as the sole product the rearranged tribromide